

A Mean Atom Trajectory Model for Monatomic Liquids

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February 1, 2008

Abstract

A recent description of the motion of atoms in a classical monatomic system in liquid and supercooled liquid states divides the motion into two parts: oscillations within a given many-particle potential valley, and transit motion which carries the system from one many-particle valley to another. Building on this picture, we construct a model for the trajectory of an average atom in the system. The trajectory consists of oscillations at the normal-mode distribution of frequencies, representing motion within a fluctuating single-particle well, interspersed with position- and velocity-conserving transits to similar adjacent wells. For the supercooled liquid in nondiffusing states, the model gives velocity and displacement autocorrelation functions which exactly match those found in the many-particle harmonic approximation, and which are known to agree almost precisely with molecular dynamics (MD) simulations of liquid Na. At higher temperatures, by allowing transits to proceed at a temperature-dependent rate, the model gives velocity autocorrelation functions which are also in remarkably good agreement with MD simulations of Na at up to three times its melting temperature. Two independent processes in the model relax velocity autocorrelations: (a) dephasing due to the presence of many frequency components, which operates at all temperatures but which produces zero diffusion, and (b) the transit process, which increases with increasing temperature and which produces diffusion. Compared

to several treatments of velocity autocorrelations based on instantaneous normal modes, the present model offers an advantage: It provides a single-atom trajectory in real space and time, including transits and valid for arbitrary times, from which all single-atom correlation functions can be calculated, and they are also valid at all times.

1 Introduction

The motion of atoms in a liquid can be divided into two constituent parts: (a) oscillation in a valley of the liquid’s many-body potential and (b) transits between many-body valleys. The latter process is responsible for self-diffusion. As we showed in a previous paper [1], which drew upon earlier results of Clements and Wallace [2, 3], the former motion can be modeled very precisely under the assumption that the valleys are nearly harmonic, with the majority of valleys (the random valleys) sharing a common spectrum of frequencies. Specifically, a purely harmonic model provides an extremely accurate formula for $\hat{Z}(t)$, the normalized velocity autocorrelation function, in the nondiffusing regime. Here we will use this picture and our previous work to justify a “mean atom trajectory” model, a single-atom model that approximates the behavior of an average atom in the liquid and correctly reproduces its nondiffusing behavior. Then we will introduce a simple intuitive account of the transit process that allows us to extend the model to the self-diffusing regime. In Sec. 2 we develop this model and explain how it is used to calculate $\hat{Z}(t)$ for a diffusing liquid. Then we fit the model to MD simulations at various temperatures in Sec. 3, and we comment on the quality of the results. In Sec. 4 we compare the present mean atom trajectory model with previous work based on Instantaneous Normal Modes (INM), and with an earlier independent atom model [4], and we summarize our conclusions.

2 The Mean Atom Trajectory Model

2.1 General comments

To form an appropriate basis for our model, we must begin with some initial reasonable approximations about the nature of the valleys and transits in the real liquid. As mentioned in the Introduction, available evidence suggests that the valleys are nearly harmonic, and we will continue to assume

that here. Further, we will assume that transits between valleys occur instantaneously and are local in character; that is, each transit involves only a few neighboring atoms.

Now for the nondiffusing supercooled liquid, there are no transits, and as we've seen the system's motion is accurately expressed in terms of the harmonic normal modes. But it is also legitimate to consider this motion from the point of view of a single atom, and when we do so we see that each atom moves along a complicated trajectory within a single-particle potential well which fluctuates because of the motion of neighboring atoms, but whose center is fixed in space. An important timescale for this motion is the single-atom mean vibrational period τ , which we take as $2\pi/\omega_{\text{rms}}$, where ω_{rms} is the rms frequency of the set of normal modes. Let us now follow the single-atom description as the temperature is increased. Once the glass transition is passed, the atom will begin to make transits from one single-particle well to another [5], and even before the melting temperature is reached, the transit rate will be on the order of one per mean vibrational period. Since each atom has approximately ten neighbors, roughly ten transits will occur in its immediate vicinity every period, changing the set of normal mode eigenvectors each time; thus we conclude that a decomposition of the motion into normal modes will not be useful when the liquid is diffusing, so we have no choice but to follow a single-atom description for the liquid state [4]. That being the case, we shall start from the beginning with a single-atom description, in order to construct a unified model for diffusing and nondiffusing motion alike.

2.2 Nondiffusing regime

Our starting point will be in the nondiffusing regime, where a normal mode analysis is still valid. As shown in [1], the i th coordinate of the K th atom in an N -body harmonic valley can be written

$$u_{Ki}(t) = \sum_{\lambda} w_{Ki,\lambda} a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}), \quad (1)$$

where the $w_{Ki,\lambda}$ form a $3N \times 3N$ orthogonal matrix, the ω_{λ} are the frequencies of the normal modes, and the a_{λ} are the amplitudes of the modes. Three of the modes have zero frequency and correspond to center of mass motion; here we demand that the center of mass is stationary, so the system has only $3N - 3$ independent degrees of freedom, the zero frequency modes are absent,

and the sum over λ runs from 1 to $3N - 3$. To make this an equation for a “mean” atom, we first drop the index K :

$$u_i(t) = \sum_{\lambda} w_{i\lambda} a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}). \quad (2)$$

Now we must reinterpret the $w_{i\lambda}$ since they no longer form an orthogonal (or even square) matrix. Let

$$\mathbf{w}_{\lambda} = w_{1\lambda} \hat{\mathbf{x}} + w_{2\lambda} \hat{\mathbf{y}} + w_{3\lambda} \hat{\mathbf{z}} \quad (3)$$

so

$$\mathbf{u}(t) = \sum_{\lambda} \mathbf{w}_{\lambda} a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}). \quad (4)$$

We will ultimately consider situations in which the well center is allowed to move, so let $\mathbf{r}(t)$ be the atom’s position, \mathbf{R} be the location of the center of the well, and $\mathbf{u}(t)$ be the atom’s displacement from the well center; then

$$\mathbf{r}(t) = \mathbf{R} + \sum_{\lambda} \mathbf{w}_{\lambda} a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}) \quad (5)$$

with velocity

$$\mathbf{v}(t) = \sum_{\lambda} \mathbf{w}_{\lambda} a_{\lambda} \omega_{\lambda} \cos(\omega_{\lambda} t + \alpha_{\lambda}). \quad (6)$$

We now have the basic formula, but we must decide how to assign values to the \mathbf{w}_{λ} , a_{λ} , and α_{λ} . Let’s do this by calculating $Z(t)$, the velocity auto-correlation function, in this model and comparing it to the harmonic result derived in [1].

$$\begin{aligned} Z(t) &= \frac{1}{3} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \\ &= \frac{1}{3} \sum_{\lambda\lambda'} \mathbf{w}_{\lambda} \cdot \mathbf{w}_{\lambda'} a_{\lambda} a_{\lambda'} \omega_{\lambda} \omega_{\lambda'} \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda'}) \rangle \end{aligned} \quad (7)$$

Let’s assign the α_{λ} randomly and average over each α_{λ} *separately*; then if $\lambda \neq \lambda'$,

$$\langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda'}) \rangle = \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \rangle \langle \cos(\alpha_{\lambda'}) \rangle = 0 \quad (8)$$

but if $\lambda = \lambda'$, then

$$\langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda'}) \rangle = \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda}) \rangle = \frac{1}{2} \cos(\omega_{\lambda} t). \quad (9)$$

Thus the $\lambda \neq \lambda'$ terms in Eq. (7) are eliminated and we have

$$Z(t) = \frac{1}{6} \sum_{\lambda} |\mathbf{w}_{\lambda}|^2 a_{\lambda}^2 \omega_{\lambda}^2 \cos(\omega_{\lambda} t). \quad (10)$$

Note that the formula for $Z(t)$ in the harmonic theory also lacks off-diagonal terms [1], but for a different reason: The orthogonality of the matrix $w_{Ki,\lambda}$ removes them in that case. Now let us make the assignment

$$\mathbf{w}_{\lambda} = \frac{1}{\sqrt{N-1}} \hat{\mathbf{w}}_{\lambda} \quad (11)$$

where $\hat{\mathbf{w}}_{\lambda}$ is a randomly chosen unit vector; then

$$Z(t) = \frac{1}{6N-6} \sum_{\lambda} a_{\lambda}^2 \omega_{\lambda}^2 \cos(\omega_{\lambda} t). \quad (12)$$

This is the same expression for $Z(t)$ that one derives in the harmonic model (see Eq. (10) of [1]) for *any* distribution of normal mode amplitudes a_{λ} , not just the thermal equilibrium distribution. Thus our model with these choices of α_{λ} and \mathbf{w}_{λ} correctly reproduces $Z(t)$ for any equilibrium or nonequilibrium ensemble in the harmonic theory. To recover the equilibrium result, we make the final substitution

$$a_{\lambda} = \sqrt{\frac{2kT}{M\omega_{\lambda}^2}} \quad (13)$$

with the result

$$Z(t) = \frac{1}{3N-3} \frac{kT}{M} \sum_{\lambda} \cos(\omega_{\lambda} t), \quad (14)$$

which is Eq. (13) from [1]. Thus our model assumes that the motion of a mean nondiffusing atom in thermal equilibrium at temperature T is given by

$$\mathbf{r}(t) = \mathbf{R} + \frac{1}{\sqrt{N-1}} \sqrt{\frac{2kT}{M}} \sum_{\lambda} \hat{\mathbf{w}}_{\lambda} \omega_{\lambda}^{-1} \sin(\omega_{\lambda} t + \alpha_{\lambda}) \quad (15)$$

where the phases α_{λ} and unit vectors $\hat{\mathbf{w}}_{\lambda}$ are randomly chosen.

By construction this model gets the same result for $Z(t)$, and thus $\langle v^2 \rangle$, as the harmonic model; does it correctly reproduce any other functions? We can check by calculating the analog of $Z(t)$ for positions, $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$. Using

Eq. (1) for $u_{Ki}(t)$ and calculating for the harmonic model as in [1], and using Eq. (2) for $\mathbf{u}(t)$ and calculating as above, one finds in both cases that

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \frac{1}{2N-2} \sum_{\lambda} a_{\lambda}^2 \cos(\omega_{\lambda} t). \quad (16)$$

Again the substitution $a_{\lambda} = \sqrt{2kT/M\omega_{\lambda}^2}$ recovers the correct thermal equilibrium result. So this model correctly reproduces $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ and $\langle u^2 \rangle$ as well. Notice that because we have a closed form for $\mathbf{u}(t)$, all of the correlation functions calculated so far also have a closed form. Once we introduce transits, this will no longer be the case.

While this model compares well with the harmonic model, one might wonder how well it compares with molecular dynamics (MD) results. In Fig. 1 a graph of v^2 as a function of t for the model in equilibrium at 6.69 K is compared to a randomly chosen particle from an MD run of liquid Na also at 6.69 K, a temperature at which it is known the sample is nondiffusing (see [1] for details). Note that in both graphs v^2 has approximately the same amplitude, and the gaps between peaks are roughly the same size, indicating oscillations at frequencies in the same ranges. Thus not only functions of the motion but the motion itself shows strong qualitative agreement with MD in the nondiffusing regime.

The MD system with which we will be comparing our model has $N = 500$ particles, so it has 1497 normal mode frequencies. (Remember that the zero frequency modes are removed at the start.) When we introduce transits, we will have to evaluate $Z(t)$ numerically, and for speed of computation we would like to use only a representative subset of the normal mode frequencies, say 75 instead of all 1497. The original set of frequencies is determined as described in [1]. We decided which subset to use by calculating three moments of the full frequency distribution defined below:

$$\begin{aligned} \omega_2 &= \left[\frac{5}{3} \langle \omega_{\lambda}^2 \rangle \right]^{1/2} \\ \omega_0 &= \exp \langle \ln(\omega_{\lambda}) \rangle \\ \omega_{-2} &= \left[\frac{1}{3} \langle \omega_{\lambda}^{-2} \rangle \right]^{-1/2}. \end{aligned} \quad (17)$$

Note that by this definition $\omega_{\text{rms}} = \sqrt{3/5} \omega_2$. We then calculated the same three moments for several sets of 75 frequencies evenly spaced throughout

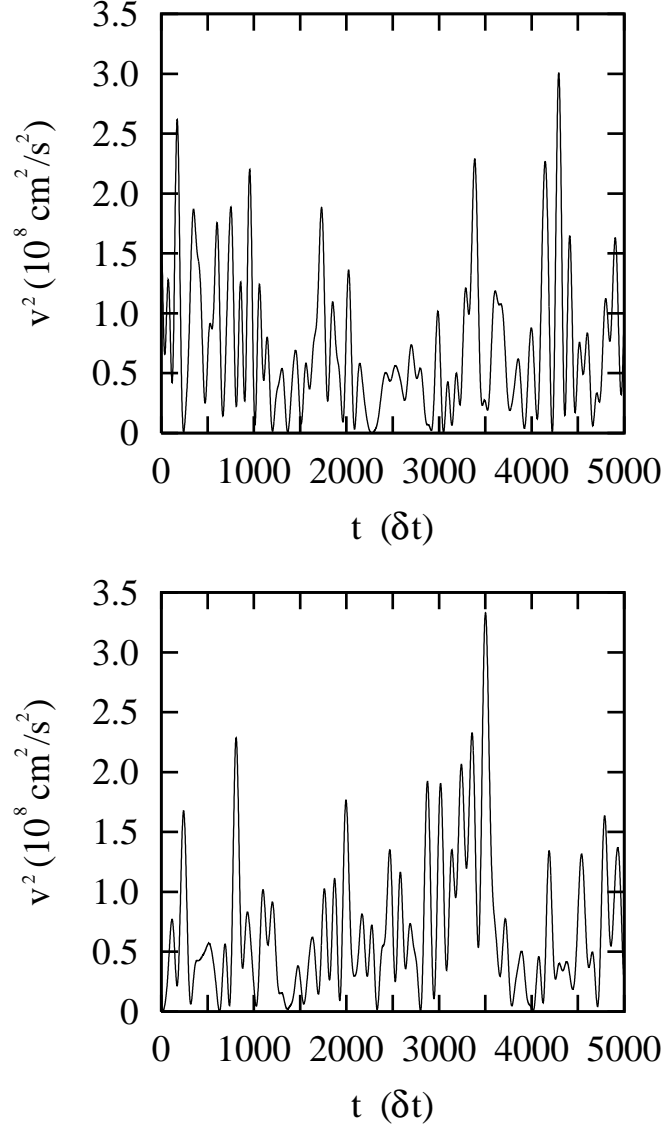


Figure 1: v^2 for a randomly chosen atom in an MD simulation of Na at 6.69 K (top) is compared with v^2 for the mean atom trajectory model in the nondiffusing regime (bottom) over 5000 timesteps of duration $\delta t = 1.4 \times 10^{-15}$ s. Notice that both fluctuations have roughly the same magnitude and oscillate at approximately the same frequencies.

the full set, and we chose the set that best fit the moments to use in further calculations. This process is somewhat subjective, because skewing the sample in favor of lower frequencies improves the accuracy of ω_{-2} but reduces the accuracy of ω_2 , and the opposite is true if one skews in favor of high frequencies. The table below shows the values of the moments for the full set and the reduced set of 75 that we ultimately chose. The frequencies are in units of δt^{-1} , where $\delta t = 1.4 \times 10^{-15}$ s is the timestep of our MD simulations [1].

	Full	Reduced
ω_2	0.02826	0.02824
ω_0	0.01807	0.01803
ω_{-2}	0.02101	0.02111

To use the reduced set we must rewrite our formulas for $\mathbf{r}(t)$ and $\mathbf{v}(t)$ slightly. Let Λ be the total number of frequencies; then $\Lambda = 3N - 3$ for the full set so $\mathbf{r}(t)$ and $\mathbf{v}(t)$ become

$$\begin{aligned}
\mathbf{r}(t) &= \mathbf{R} + \sqrt{\frac{3}{\Lambda}} \sqrt{\frac{2kT}{M}} \sum_{\lambda=1}^{\Lambda} \hat{\mathbf{w}}_{\lambda} \omega_{\lambda}^{-1} \sin(\omega_{\lambda} t + \alpha_{\lambda}) \\
\mathbf{v}(t) &= \sqrt{\frac{3}{\Lambda}} \sqrt{\frac{2kT}{M}} \sum_{\lambda=1}^{\Lambda} \hat{\mathbf{w}}_{\lambda} \cos(\omega_{\lambda} t + \alpha_{\lambda}).
\end{aligned} \tag{18}$$

This form is also correct for the reduced set of frequencies ω_{λ} , so this is the form we will use. As another check on the accuracy of our results with only 75 frequencies, we recalculated the original $\sum \cos(\omega_{\lambda} t)$ expression for $\hat{Z}(t)$ using both the full and reduced sets; their disagreement is at most 0.01 out to time $1000 \delta t$. However, the discrepancy grows beyond that time, as the expression using the reduced set begins to experience revivals. Hence we will not consider $\hat{Z}(t)$ beyond that point.

2.3 Diffusing regime

To incorporate diffusion into the mean atom trajectory model, we rely on Wallace's notion of a single-particle transit [6], a nearly instantaneous transition from one well to another. As discussed in [5], we expect transits to be governed not by thermal activation (having enough energy to escape a fixed well) but by *correlations* (neighbors must be positioned properly for a

low-potential path to open between wells). We implement this property by having transits occur at a temperature dependent *rate* $\nu(T)$, so in a small time interval Δt the probability of a single transit is $\nu\Delta t$.

We model the transit process itself by assuming it occurs instantaneously in the forward direction; from this we can determine the parameters \mathbf{R} , $\hat{\mathbf{w}}_\lambda$, and α_λ appearing in Eq. (18) after the transit in terms of the same quantities before the transit. Since the process is instantaneous, both $\mathbf{r}(t)$ and $\mathbf{v}(t)$ are the same before and afterwards. Let $\mathbf{R}^{\text{before}}$ and $\mathbf{R}^{\text{after}}$ be the well centers before and after the transit and let $\mathbf{u}^{\text{before}}$ and $\mathbf{u}^{\text{after}}$ be the corresponding displacements from the well centers. Then $\mathbf{r}^{\text{before}} = \mathbf{r}^{\text{after}}$ implies

$$\mathbf{R}^{\text{before}} + \mathbf{u}^{\text{before}} = \mathbf{R}^{\text{after}} + \mathbf{u}^{\text{after}}. \quad (19)$$

To transit *forward*, we assume the center of the new well lies along the line between the old well center and the atom, but it lies on the opposite side of the atom from the old well center an equal distance away. This implies $\mathbf{u}^{\text{after}} = -\mathbf{u}^{\text{before}}$, so

$$\mathbf{R}^{\text{before}} + \mathbf{u}^{\text{before}} = \mathbf{R}^{\text{after}} - \mathbf{u}^{\text{before}} \quad (20)$$

with the result

$$\mathbf{R}^{\text{after}} = \mathbf{R}^{\text{before}} + 2\mathbf{u}^{\text{before}}. \quad (21)$$

This determines the new well center in terms of the coordinates before the transit. As for the unit vectors $\hat{\mathbf{w}}_\lambda$, since they are randomly generated and play no role in calculating $\hat{Z}(t)$, we have decided to leave them unchanged by transits. Finally, we have the phases α_λ . We must use these to implement the relations

$$\mathbf{u}^{\text{after}} = -\mathbf{u}^{\text{before}}, \quad \mathbf{v}^{\text{after}} = \mathbf{v}^{\text{before}} \quad (22)$$

which we have assumed above. Since $\mathbf{u}(t)$ is a sum of sines and $\mathbf{v}(t)$ a sum of cosines, the simplest way to change the sign of $\mathbf{u}(t)$ while preserving that of $\mathbf{v}(t)$ is to reverse the signs of the arguments $(\omega_\lambda t + \alpha_\lambda)$ in Eq. (18). Let the transit occur at time t_0 ; then

$$\omega_\lambda t_0 + \alpha_\lambda^{\text{after}} = -(\omega_\lambda t_0 + \alpha_\lambda^{\text{before}}) \quad (23)$$

so

$$\alpha_\lambda^{\text{after}} = -2\omega_\lambda t_0 - \alpha_\lambda^{\text{before}}. \quad (24)$$

Thus, in this model a transit is implemented at time t_0 by leaving the $\hat{\mathbf{w}}_\lambda$ alone and making the substitutions

$$\begin{aligned}\mathbf{R} &\rightarrow \mathbf{R} + 2\mathbf{u}(t_0) \\ \alpha_\lambda &\rightarrow -2\omega_\lambda t_0 - \alpha_\lambda.\end{aligned}\tag{25}$$

This conserves \mathbf{r} , reverses the sign of \mathbf{u} , and conserves \mathbf{v} .

Now our mean atom trajectory model consists of nondiffusive motion between transits as given by Eq. (18), with a given probability in each small time interval that \mathbf{R} and the phases α_λ will be replaced with new values as determined in Eq. (25). The addition of transits means that we no longer have closed form expressions for $\mathbf{r}(t)$ and $\mathbf{v}(t)$ for all times, so we have no closed form expression for $\hat{Z}(t)$; but this model can be implemented easily on a computer in a manner analogous to an MD calculation, and in that way we can calculate autocorrelation functions. We turn to that calculation next.

2.4 Evaluating $\hat{Z}(t)$ in the diffusing regime

To calculate $\hat{Z}(t)$, we select a value for the rate ν , generate a random set of $\hat{\mathbf{w}}_\lambda$ and α_λ , and use Eq. (18) to calculate $\mathbf{r}(t)$ and $\mathbf{v}(t)$ from $t = 0$ to $t = t_{\max}$ in increments of δt , where the criterion for choosing t_{\max} is discussed below and δt is the timestep used in our MD simulations (defined in Subsection 2.2). At each timestep, we check to see if a transit occurs, and if so we implement Eq. (25) and continue with the new \mathbf{R} and α_λ . We then calculate $\hat{Z}(t)$ using the formula

$$Z(t) = \frac{1}{3(t_{\max} - t) + 3} \sum_{t'=0}^{t_{\max}-t} \mathbf{v}(t+t') \cdot \mathbf{v}(t') \tag{26}$$

and normalizing. This equation is a modified form of the expression used to calculate $Z(t)$ in MD; notice that the average over t' has the same effect as averaging separately over each phase α_λ that appears in the velocity vectors. Just as in MD, we want to average over a large data set, so we require $t_{\max} \gg t$; we have chosen $t_{\max} = 20$ million timesteps and we calculate $\hat{Z}(t)$ only to $t = 1000$ timesteps. We estimate the total error from using only a subset of all 1497 frequencies and the finite size of the data set to be at most 0.01; in particular, when $\nu = 0$ the calculation converges to the closed form result $\sum \cos(\omega_\lambda t)$ to this accuracy.

3 Comparison with MD

The MD setup with which we compared the predictions of this model is the one described in [1]; $N = 500$ atoms of Na move under the influence of a highly realistic pair potential with the timestep $\delta t = 1.4 \times 10^{-15}$ given in Subsection 2.2. We performed equilibrium runs of the system at 216.3 K, 309.7 K, 425.0 K, 664.7 K, and 1022.0 K, all temperatures at which the system is diffusing. Since $T_m = 371.0$ K for Na at this density, our simulations range from the supercooled regime to nearly three times the melting temperature. We then ran the model for various values of ν , adjusting until the model matched the value of the first minimum of $\hat{Z}(t)$ at each temperature. The values of ν that we fit for all temperatures are given below, and the resulting $\hat{Z}(t)$ for each ν is compared to the corresponding MD result in Figs. 2 through 6. Here ν is expressed in units of τ^{-1} where $\tau = 2\pi/\omega_{\text{rms}}$ is the single-atom mean vibrational period defined in Subsection 2.1.

T (K)	ν (τ^{-1})
216.3	0.35018
309.7	0.60276
425.0	0.83985
664.7	1.24858
1022.0	1.68774

Notice that in all cases ν is of the same order of magnitude as τ^{-1} , indicating roughly one transit per mean vibrational period, as mentioned in Subsection 2.1, and as predicted in [5].

The most obvious trend exhibited by $\hat{Z}(t)$ from the five MD runs is that its first minimum is rising with increasing T ; as we mention below, this is the primary reason for the increasing diffusion coefficient D . Note that the model is able to reproduce this most important feature quite satisfactorily. In fact, all five fits of the model to the MD results capture their essential features, but we do see systematic trends in the discrepancies. First, note that the location of the first minimum barely changes at all in the model as ν is raised, but in MD the first minimum moves steadily to earlier times as the temperature rises. The first minimum occurs at a time roughly equal to half of the mean vibrational period ($\tau = 287 \delta t$ in this system), so the steady drift backward suggests that the MD system is sampling a higher range of frequencies at higher T . Also, for the three lowest temperatures the model tends to overshoot the MD result in the vicinity of the first two maxima after

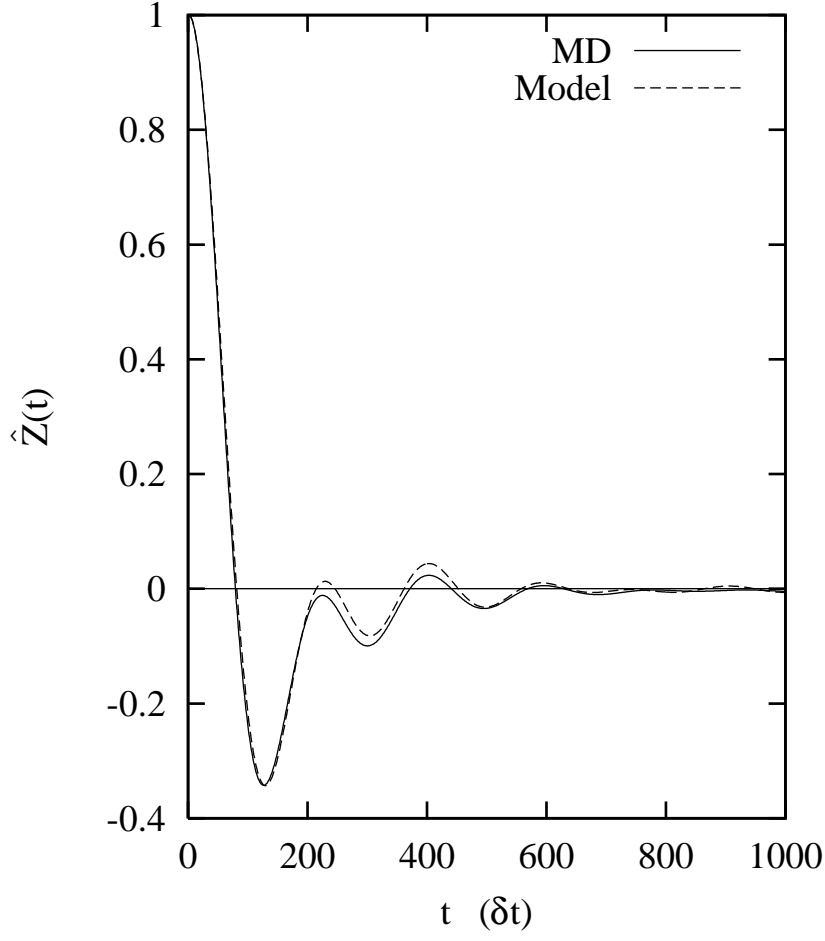


Figure 2: The model prediction for $\hat{Z}(t)$ at $\nu = 0.35018 \tau^{-1}$ compared with the MD result for supercooled liquid Na at $T = 216.3$ K.

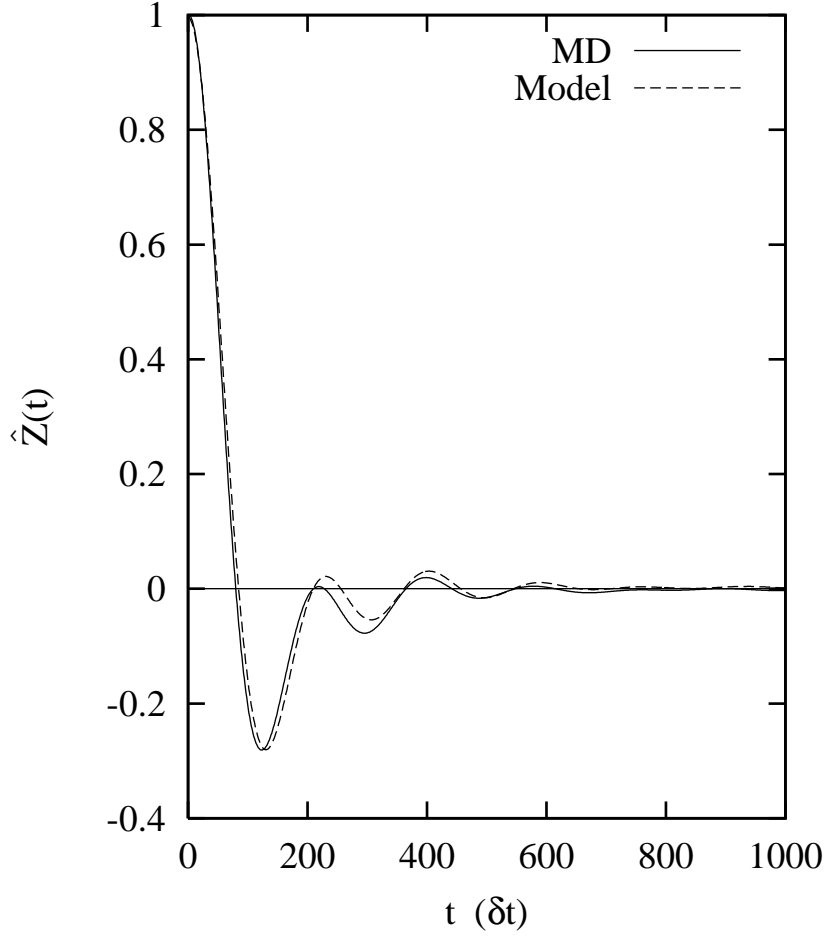


Figure 3: The model prediction for $\hat{Z}(t)$ at $\nu = 0.60276 \tau^{-1}$ compared with the MD result for supercooled liquid Na at $T = 309.7$ K.

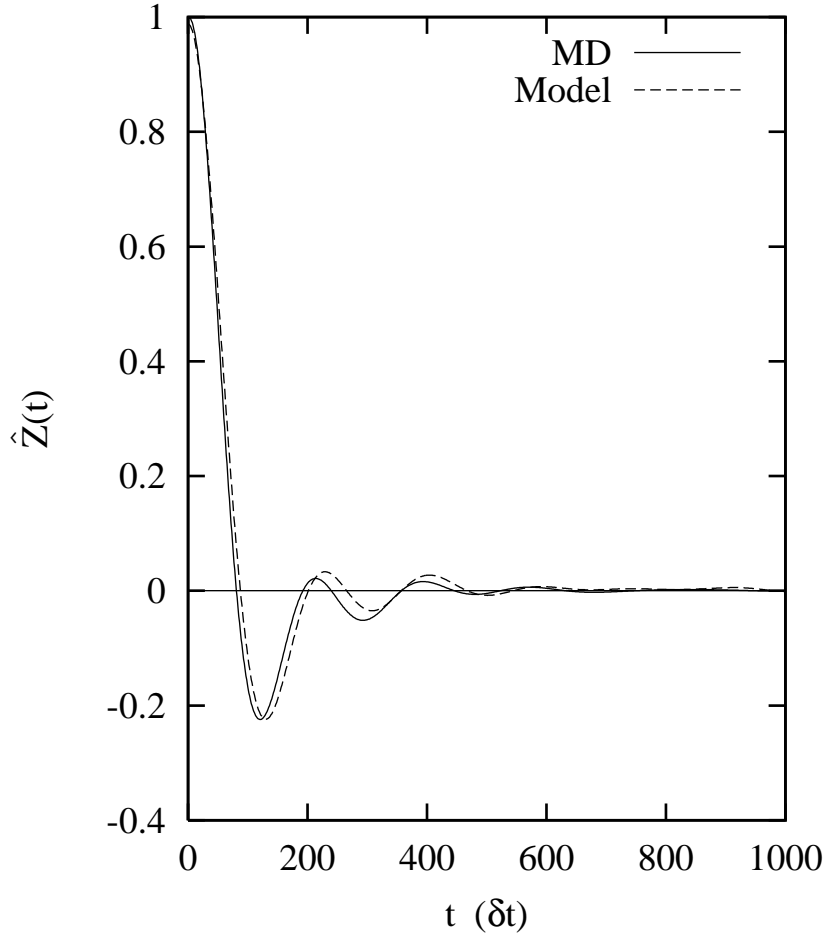


Figure 4: The model prediction for $\hat{Z}(t)$ at $\nu = 0.83985 \tau^{-1}$ compared with the MD result for liquid Na at $T = 425.0$ K.

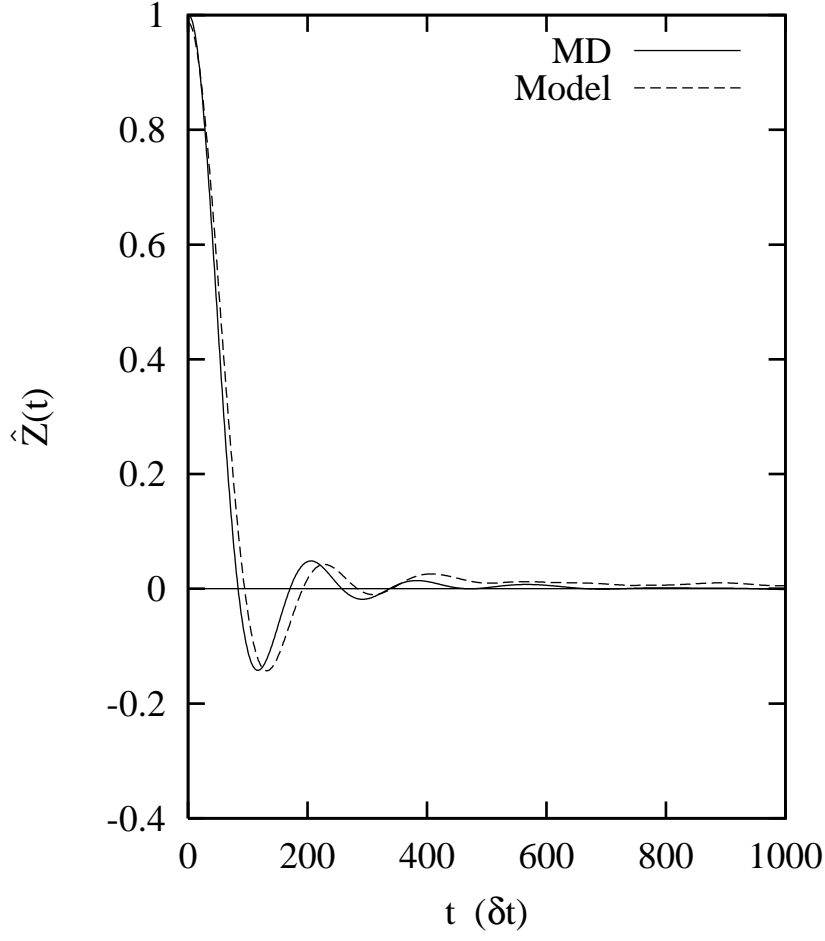


Figure 5: The model prediction for $\hat{Z}(t)$ at $\nu = 1.24858 \tau^{-1}$ compared with the MD result for liquid Na at $T = 664.7$ K.

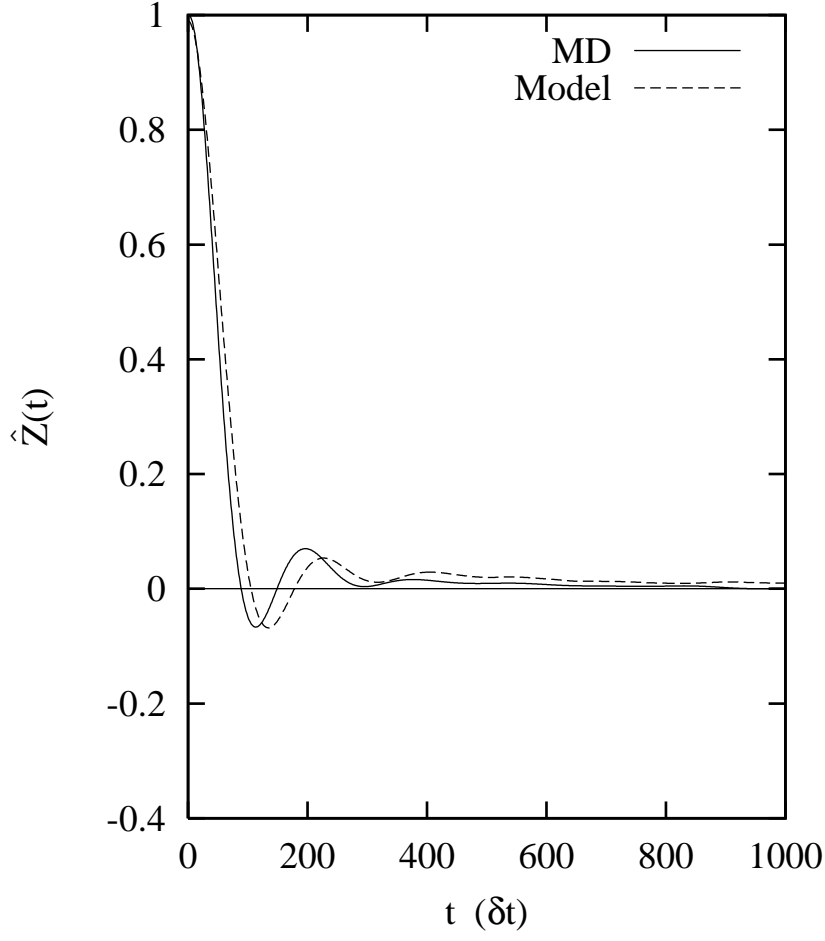


Figure 6: The model prediction for $\hat{Z}(t)$ at $\nu = 1.68774 \tau^{-1}$ compared with the MD result for liquid Na at $T = 1022.0$ K.

the origin, and at the highest two temperatures this overshoot is accompanied by a positive tail that is slightly higher than the (still somewhat long) tail predicted by MD. These overshoots should clearly affect the diffusion coefficient D , which is the integral of $Z(t)$. To check this, we calculated the reduced diffusion coefficient \hat{D} , the integral of $\hat{Z}(t)$, which is related to D by

$$D = \frac{kT}{M} \hat{D}. \quad (27)$$

The results are compared to the values of \hat{D} calculated from the MD runs in Fig. 7. The results from the two nondiffusing runs discussed in [1] are also included. In all of the diffusing cases, the model overestimates \hat{D} by roughly the same amount, which we take to be the effect of the overshoots at the first two maxima. At the higher temperatures the discrepancy is also higher, presumably due to the model's long tail.

It is interesting to note that this MD system produces results that agree very closely with experiment: For example, the MD predicts that at $T = 425.0$ K and $\rho = 0.925$ g/cm³, $D = 6.40 \times 10^{-5}$ cm²/s, while experiments by Larsson, Roxbergh, and Lodding [7] find that at $T = 425.0$ K and $\rho = 0.915$ g/cm³, $D = 6.020 \times 10^{-5}$ cm²/s. Hence our agreement with MD results genuinely reflects agreement with properties of real liquid Na.

4 Conclusions

We have presented a single-atom model of a monatomic liquid that provides a unified account of diffusing and nondiffusing behavior. The nondiffusing motion is modeled as a sum of oscillations at the normal mode frequencies (Eq. (18)), simulating the trajectory of an average atom in a complicated single-body potential well that fluctuates due to the motion of its neighbors. Self-diffusion is accounted for in terms of instantaneous transits between wells, which occur at a temperature-dependent rate ν . Since this model gives a simple and straightforward account of the motion itself, it can easily be used to calculate any single-atom correlation function one wishes; here we have focussed on the velocity autocorrelation function. It is interesting to note that in this model the velocity correlations persist through a transit, instead of being washed out entirely by the transit process; we will return to this point below. The relaxation of correlations seen by the decay of $\hat{Z}(t)$ arises here from two distinct processes: Dephasing as a result of the

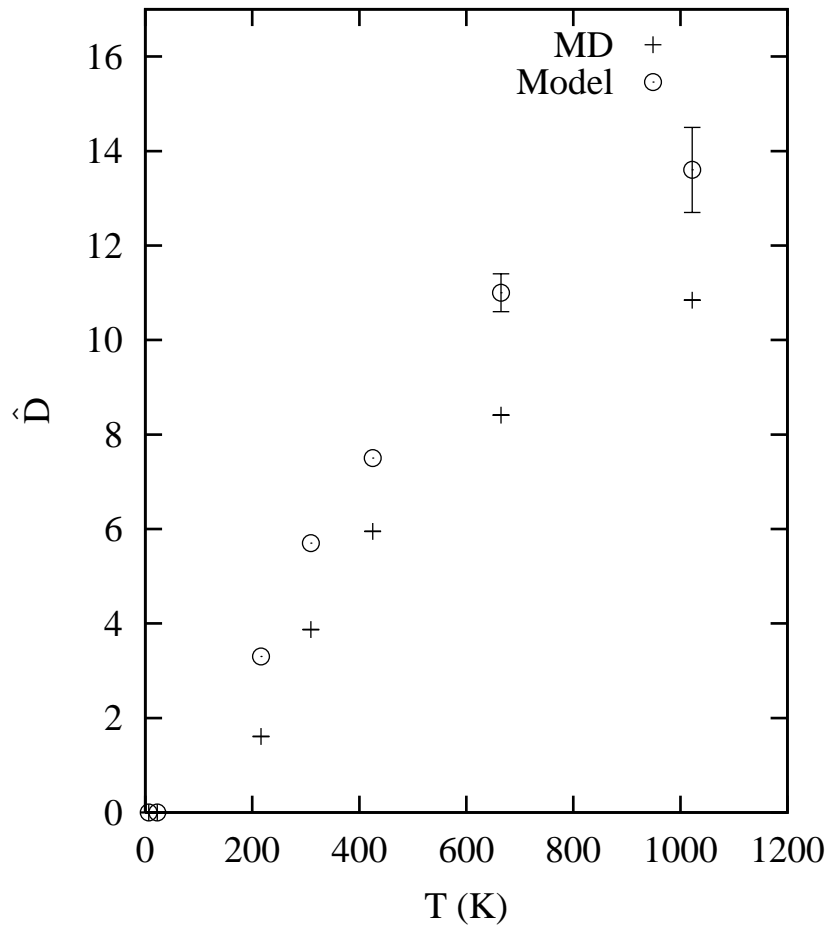


Figure 7: \hat{D} as a function of T for both the model and MD.

large number of frequencies in the single-well motion, and transits between wells. The dephasing effect produces relaxation but not diffusion: It causes $\hat{Z}(t)$ to decay [1] but its integral remains zero. On the other hand, transits certainly contribute to relaxation (see [4], where they provide the only relaxation mechanism), but in addition they raise the first minimum of $\hat{Z}(t)$ substantially, increasing its integral and providing a nonzero D .

The comparison of this model to MD results is generally quite positive, particularly for a one-parameter model; the two calculations of $\hat{Z}(t)$ agree strongly over 1000 timesteps. In addition, the match is encouraging over a very large range of temperatures, from essentially 0 K to $3T_m$. The most noticeable discrepancies are the backward drift in the location of the first minimum of $\hat{Z}(t)$, which is present in MD but not the model, and the tendency of the model to exaggerate certain characteristics of the MD results (the maxima at intermediate times and the high- T positive tail). This latter effect is responsible for the model's overestimate of the diffusion coefficient, though we hasten to add that the model \hat{D} is still in satisfactory agreement with MD results, especially for the liquid at $T \geq T_m$ (see Fig. 7).

As in [1], it is useful to compare this model and the accompanying results to the work others have done using the formalism of Instantaneous Normal Modes (INM) and similar methods. Previously, we discussed the advantages of our general approach and the superior quality of its results when applied to nondiffusing states; here we will consider matters relating explicitly to mechanisms of diffusion. As is noted explicitly by Vallauri and Bermejo [8], the account of INM by Stratt (see, for example, [9]) does not consider diffusion at all; their $Z(t)$ is essentially a sum over cosines, and as such it integrates to zero. This is understandable, because as Stratt et al. repeatedly emphasize, their approximation is valid only for very short times, so they are not attempting to model effects with longer timescales. They compare their INM results with MD calculations of $\hat{Z}(t)$ for states of an LJ system ranging from a moderately supercooled liquid to well above the melting temperature, and our fits are of roughly the same quality or better in all cases. Authors who do attempt to model diffusion usually follow the path suggested initially by Zwanzig [10], who thought of the liquid's phase space as divided into "cells" in which each atom spends its time before finding a saddle point in the potential and jumping from one cell to the next. He imagined as a first approximation that the jumps destroy all correlations between the cells; since atoms are jumping all the time, he suggested that the net result was to multiply the nondiffusing form of $Z(t)$ by a damping factor $\exp(-t/\tau)$ for

some timescale τ representing the lifetime of a stay in a single cell. Notice that Zwanzig provided no dynamical model of the jumping process itself. This suggestion has been developed and transformed extensively by Madan, Keyes, and Seeley [11], who take a general Zwanzig-like functional form for $Z(t)$ and use a combination of heuristic arguments and constraints on its moments to specify its dependence on a “hopping rate” ω_v , the analog of τ^{-1} for Zwanzig, which they then extract from the unstable lobe of the INM spectrum. Although we cannot be entirely sure, as indicated in [1], we think it most likely that their simulations of LJ Ar at 80 K, 120 K, and 150 K consist of states comparable to our Figs. 2 and 3, and again we would argue that our fits are somewhat better. Finally, Cao and Voth [12] also approach diffusion by means of a damping factor, and they consider factors of two different types, each of which contains parameters that can be determined from other calculated or experimental quantities. Their matches with MD are actually quite good, but again ours are of at least comparable quality.

Having claimed that our matches to MD simulations are as good as or better than all of the others we have surveyed, let us emphasize a fundamental difference between our approaches to diffusion: We provide an account of the *process* of transiting from well to well, so we have a model of the actual *motion* of a mean atom in space that is valid to arbitrary times, and given this model we can *calculate* the effect of transits on correlations. All other approaches we know of begin with an account of the motion valid only for very short times, calculate $Z(t)$ from this motion, and then try to model the effects of diffusion on $Z(t)$ directly, using parameters that are thought to be characteristic of jumps between wells. In the diffusing regime, no one else we have seen actually calculates $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ to find $Z(t)$, as we do. In the process, we find that some of the assumptions made by others, in particular Zwanzig’s hypothesis that jumps between wells simply erase correlations, are not true. This approach is already yielding insights into the actual motion of an atom undergoing a transit.

Finally, we would like to compare the present mean atom trajectory model with an earlier independent atom model by Wallace [4]. In developing the independent atom model, two arguments were made: (a) the high rate of transits in the liquid state shows the need to abandon the normal mode description of motion, and instead picture the motion of a single atom among a set of fluctuating wells, and (b) the leading approximation to a fluctuating well is its smooth time average well. Accordingly, the independent atom oscillates with frequency ω in a smooth isotropic well, and it transits with

probability μ to an adjacent identical well at each turning point [4]. What we have now learned by considering low temperatures, and especially the nondiffusing states of [1], is that the MD system exhibits a velocity decorrelation process which results from the presence of many frequencies in the single-particle motion, making assumption (b) less reasonable. In the current model these many frequencies are retained, and they are intended to represent the strong fluctuations in each single-particle well; in this way the current model makes an important improvement over the independent atom model, where the well fluctuations were averaged out. Beyond this difference, the two models contain similar but not identical treatments of transits, whose rate increases with increasing temperature, and which produce self-diffusion. The less detailed but simpler independent atom model has proven useful in a description of the glass transition [5], and the corresponding transit parameter has been used to relate shear viscosity and self-diffusion in liquid metals [13].

The next logical step in this work, given the results so far, is to extend the mean atom trajectory model and apply it to calculations of more complicated correlation functions of the liquid's motion.

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